



An in situ generated carbon as integrated conductive additive for hierarchical negative plate of lead-acid battery



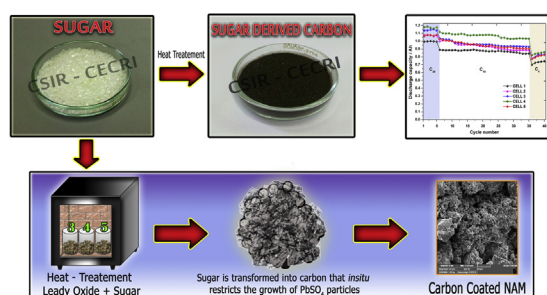
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HIGHLIGHTS

- The sugar derived carbon added negative electrode exhibits excellent performance.
- In-situ coating of sugar derived carbon prevents formation of irreversible PbSO_4 .
- The unique structure endows the high-rate transportation of electrons.
- The charge acceptance of the test cell is also enhanced.
- A new pathway to fabricate promising negative electrode for lead-acid batteries.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we report an in situ generated carbon from sugar as additive in the Negative Active Mass (NAM) which enhances the charge–discharge characteristics of the lead-acid cells. In situ formed sugar derived carbon (SDC) with lead oxide (LO) provides a conductive network and excellent protection against NAM irreversible lead sulfation. The effect of SDC and carbon black (CB) added negative plates are characterized by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), galvanostatic charge–discharge, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), respectively. The results show that subtle changes in the addition of carbon to NAM led to subsequent changes on the performance during partial-state-of-charge (PSoc) operations in lead-acid cells. Furthermore, SDC added cells exhibit remarkable improvement in the rate capability, active material utilization, cycle performance and charge acceptance compared to that of the conventional CB added cells. The impact of SDC with LO at various synthesis conditions on the electrochemical performance of the negative plate is studied systematically.

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1. Introduction

Lead-acid battery (LAB) has been playing an active role with a long history of more than 150 years [1]. Even though, modern systems such as lithium-ion, Nickel–Metal hydride (Ni/MH)

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systems are coming up to replace LABs; still LAB is the main candidate for automotive, hybrid electric vehicles (HEV), uninterruptible power supplies (UPS), solar traffic lights, telecommunications and stationary applications [2]. The reason being, the low abundance of lithium in the earth's crust which is a serious concern on the availability of lithium if electric vehicles become the reality of the future and high efficient recycling technology could not be developed [3,4]. However, no other battery is yet able to compete with LABs on cost ground and recycling technology. The raw materials for their manufacture are practically unlimited, about 95% of

the materials can be recovered and reused. The advantages of LAB include low cost, high safety, low self-discharge and easy construction [5]. The main weakness of the LAB system is low specific energy, negative plate sulfation, and poor cyclability in PSoC application. This is due to the insufficient utilization of active mass and the discharged product of lead sulfate which has not efficiently converted back to its original form and leads to progressive accumulation of irreversible PbSO_4 on the NAM. This insulating material hinders the acid diffusion on the surface which is coupled with a loss of electrical connectivity and rapid decline in capacity. The cycle life of the batteries is determined by the reversibility of the processes that proceed during charge/discharge [6]. In this regard, much attention is now focused on NAM which must be well combined with a conductive additive and possibly the effective means of eliminating these problems.

Many efforts have been made over the past few years to improve the performance of NAM with the addition of several forms of carbon materials which can act as a barrier to protect irreversible lead sulfation and also to maintain the electronic conductivity [7–11]. Most approaches have so far addressed the dry mixing of leady oxide (LO) with carbon. However, such dry mixing incorporation affords a kind of physical binding that may break during the prolonged PSoC cycling and leads to imperfect electronic conductivity within the NAM. Besides the electronic conductivity, the additive should have chemical stability and convenient geometry to build up a conductive percolation matrix within the NAM. In contrast, few attempts, have addressed that the lead powder/carbon black and glucose composite obtained by spray drying and subsequent calcinations process, which limits the initial capacity of the test cell [12]. Recently, PbO@C nanocomposites were prepared by carbonizing lead nitrate impregnated starch at the high temperature under the nitrogen atmosphere [13].

Interestingly, none of these studies have reported in situ preparation of SDC with leady oxide. The use of SDC with leady oxide would be one of the most effective and economic methods to attain an in situ conductive formation. Carbon materials with high surface area, pore volumes, excellent chemical stability, high electrical and thermal conductivity are widely employed in energy storage and conversion [14,15]. For many years, carbon has been favoured as an additive in LAB [16–25]. Furthermore, carbon might impede the accumulation of lead sulfate crystals and the carbon particles might act as nucleation centres for crystallization of lead sulfate [26]. Moreover, carbon material arrangement/contact with lead particle within the NAM is playing a crucial role in the electrochemical performance and facilitating access of the lowest ohmic resistance of the lead–carbon contact. Consequently, besides the basic requirement of high surface area and electrical conductivity, it is indispensable to have an appropriate arrangement/contact of the carbon with active material is essential for ideal negative electrode material.

We report herein synthesizing carbon from a direct carbonization of sugar under mild solvent at low temperature with leady oxide to attain an in situ conductive formation as shown in Fig. 1. The use of sugar derived carbon is also a cost-effective way since sugar is abundantly available and thus relatively cheap chemical and environmentally friendly [27]. However, it should be noted that numerous studies involving the synthesis of heat treated, hydrothermal and solvothermally prepared PbO_2 , for positive active mass [28–31]. Several reports established the optimum methods for sugar, glucose and sucrose to make Li-ion, LiFePO_4 battery materials and supercapacitors. [32–36] However, to the best of our knowledge, there have been no reports on the in-situ generation of carbon by employing sugar coating in the field of LAB. The SDC embedded LO with various synthesis conditions is a simple way to alleviate the cyclic and PSoC performance. The dispersed SDC particles generated in situ provide pathways for

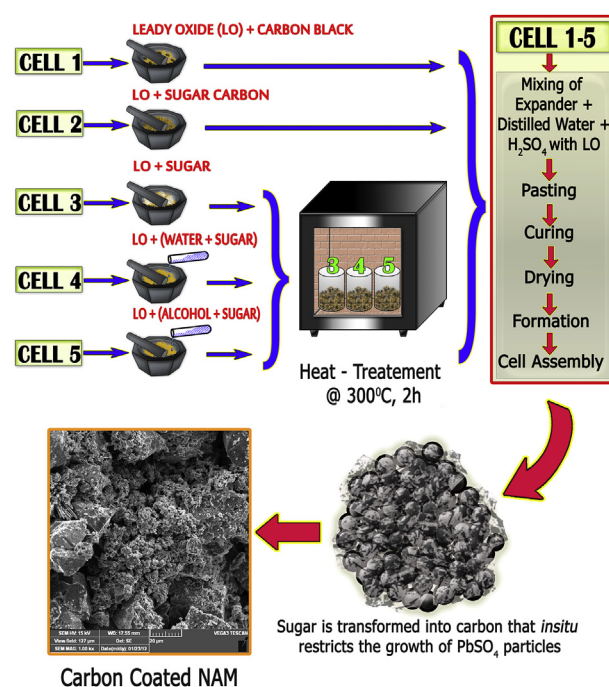


Fig. 1. Schematic illustration of preparation process for the leady oxide/sugar derived carbon material including an in situ conductive network formation.

electron transfer thus results in the improved conductivity and suppresses the irreversible lead sulfate. Moreover, high utilization of the active material and good cycling properties of the negative plate is achieved.

2. Experimental

2.1. Negative plate preparation and characterization method

Sugar was purified, dewatered and carbonized by heating in a furnace at 300 °C under air atmosphere. After 2 h, the sugar melts, decomposed and carbonised. In our study, subsequent to the heating, 1 g of sugar resulted in about 0.28 g of carbon [36]. The in-situ generation of SDC is carried out in different methods as described below:

Before dry mixing/pasting process, the leady oxide (LO) was pre-treated with sugar (Cell 3) then heated at 300 °C for 2-h. The degree of oxidation of the LO was 76%. The sugar was dissolved with an appropriate amount of water (Cell 4) and alcohol (Cell 5) then the solution was mixed with LO and heated at 300 °C for 2-h. whereas, carbon black (Cell 1) and SDC (Cell 2) was directly added with leady oxide while dry mixing process in such a case we have not heated the LO. Fig. 1 schematically shows the process involved in the synthesis of NAM with SDC. In all the synthesis condition described above, 0.25% of carbon black or equivalent amount of sugar to get 0.25% of carbon was taken. After heat treated LO/sugar carbon are subjected to dry mixing and pasting for making the negative plates. However, one more heated reference sample has been included to evaluate the thermal treatment of leady oxide alone in enhancing the cycling performance. For that heated leady oxide with CB added negative plate prepared and charge/discharge performance was evaluated (Cell 6).

The plates were cured and formed as per conventional technologies. Subsequent to the formation, the test cells were assembled with 1 negative and 2 positive plate per cell with PVC separator. The cells were filled with 30 mL of 1.26 sp. gr sulfuric acid

(H₂SO₄). The performance parameters of the test cells were limited by the negative plates.

Bitrode battery life cycle tester was used to perform the galvanostatic charge/discharge tests at various rates. The test cells were then subjected to accelerated partial-state-of-charge (APSoC) cycling to determine their cycle life. [37] After adjusting to 50% state of charge, the cells were alternately charged and discharged at 1C for 25 s and 3 s rest. (C is obtained from the discharge capacity, C₄) Cycling continued until the end of discharge voltage dropped below 1.5 V.

The crystalline phases were identified with XRD (X'pert PRO PAN) with Cu K α radiation. The morphology of the material was studied by scanning electron microscope (SEM, TESCAN). Thermogravimetric Analysis (TGA) was carried out on a SDT Q600 thermal-analysis instrument. Raman spectra were measured with a witesc confocal Raman instrument (CRM200) spectrometer using an Ar ion laser (514.5 nm). Dynamic Light Scattering (DLS) was performed on a Zetasizer Nano ZS and 4 mW He/Ne laser (632.8 nm wavelength) with scattering angle of 175°. The electrochemical characterization using cyclic voltammetry (AUTOLAB PGSTAT 30, Eco Chemie BV, Utrecht, The Netherlands) was performed on a geometric area of 1 cm² negative electrode. A platinum electrode with a large area was used as the auxiliary electrode. The reference electrode was Hg|Hg₂SO₄|1.28 g cm⁻³ H₂SO₄. All potentials in the cyclic voltammetry experiments are reported with respect to this reference electrode. Cyclic voltammetry was performed at a scan rate of 5 mV s⁻¹ in the potential range -0.5 V to -1.3 V. The electrochemical impedance spectroscopy (EIS) was performed in the frequency range of 10 mHz–100 kHz at an AC voltage of 5 mV.

3. Results and discussion

The in-situ generated SDC and CB used in the conventional cell were characterised with Raman spectroscopy which is a powerful tool for analysing carbonaceous materials [38]. Fig. 2 shows the Raman spectra of the CB and SDC. The peak located at 1355 and 1580 cm⁻¹ corresponds to the characteristics of disordered (D) band and graphitic (G) band of CB and SDC respectively. The D and G bands correspond to sp³ and sp² carbon stretching modes. The intensity ratio (I_D/I_G) of these two peaks can be used to evaluate the disorder degree of carbon material. The ratios between the intensities of D and G bands were 0.99 and 0.86, suggesting a higher degree of graphitization of SDC. Moreover, the decreasing integrated Raman intensity ratio of the D and G bands of carbon will increase the amount of graphene clusters in the structure, leading to improved electronic conductivity of the carbon [39].

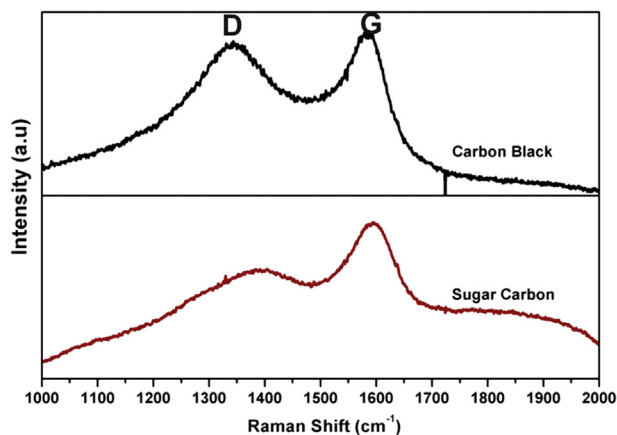


Fig. 2. (a) Raman spectra of carbon black (CB) and sugar derived carbon (SDC).

Consequently, the D band almost completely disappeared and amorphous carbon has been mostly eliminated in the SDC. This is also in agreement with XRD patterns since a sharper peak is observed for SDC (Fig. 4). A summary and specific characteristics of the SDC presented in Table 1.

All measurements were carried out in nitrogen atmosphere at a gas flow-rate of 80 mL min⁻¹ for TGA and 50 mL min⁻¹ for DSC and at constant heating rate of 5 °C min⁻¹ was chosen to determine the absorbed quantity of water and also to follow the decomposition pattern. Fig. 3a–c presents the obtained TG curves for paste raw material (without pre heat treatment), mixed dry paste and cured paste. Thermogravimetry studies in a nitrogen atmosphere on both carbon black and SDC added leady oxide had negligible mass loss as shown in Fig. 3a, which indicates that these carbons do not suffer much transformation except the decomposition of organics in carbon black and conversion of sugar to carbon. A significant weight loss was observed in the range of 200–350 °C due to the carbonisation of sugar and burning of organics. The initial small mass loss can be attributed to removal of moisture. The weight loss of the mixed dry paste and cured paste is 0.05%–0.75% within the whole range of temperatures from 35 to 500 °C, i.e. it is quite small as shown in Fig. 3b and c. Fig. 3d shows the DSC results of cured paste. The peaks at 240 °C–270 °C for the cured pastes correspond to the dehydration for 3BS which is related to the preparation method of NAM. The curve features only a sharp endothermic peak at 328 °C which is due to melting of remained unoxidized lead. In the temperature range 300 °C, this reflects basic peak for decarbonation for CB added NAM. It can be concluded that the SDC added pastes used in our experiment are not carbonated [40,41].

Fig. 4a shows the XRD pattern of carbon black and as prepared SDC material. The peak located at 26.6° was attributed to the diffraction of graphite. The broad band indicates that the structure of CB particles is amorphous. The diffraction peak obtained for CB is much lower and broader than SDC which confirm that the CB is composed of carbonaceous substances with low crystallinity. The diffraction peak for SDC shows a crystalline phase. The high crystallinity of the SDC guarantees good electrochemical performance which is proved hereinafter. Fig. 4b shows the fully formed state NAM contains small amounts of β -PbO ($2\theta = 29.08, 30.309$, d-space = 0.306 nm, 0.294 nm). Formation of β -PbO instead of Pb/PbSO₄ indicates that thermo treatment of leady oxide alter the phase transformation in the NAM. The broad diffraction peaks of β -PbO are an indication of small crystallite size. In general heat treatment of leady oxide leads to form a small amount of β -PbO is well documented in many PbO–C and metal composite reports [42–44]. Further cycling (charge/discharge), the β -PbO has been converted or partially suppressed which is observed in the XRD pattern of APSoC cycled NAM. The obtained results suggest that the SDC added NAM having the highest content of Pb is observed. Moreover the CB added NAM contains typical structure of Pb and PbSO₄.

Table 2 shows the past density, penetration and BET-surface area of the CB and the SDC added NAM. The values of paste density and penetration are slightly changed as compared with CB added NAM. During the paste mixing process sugar and SDC would react partially with sulfuric acid to produce water. This is very negligible because 0.25% of SDC added with LO. There are several methods of determining the consistency of the paste. In this study we used hemispherical cup and Globe penetrometer. The surface area of the NAM is increased in the Cell 4 compared with other cells, while CB added NAM has weakest effect. Moreover the increase of surface area of NAM subjected to plate preparation method (dispersion properties of carbon) which favours the charge acceptance and electrochemical reaction.

Fig. 5a and b shows the SEM images of carbon black and thermo treated SDC added NAM in partially formed state (after 35 h, cells

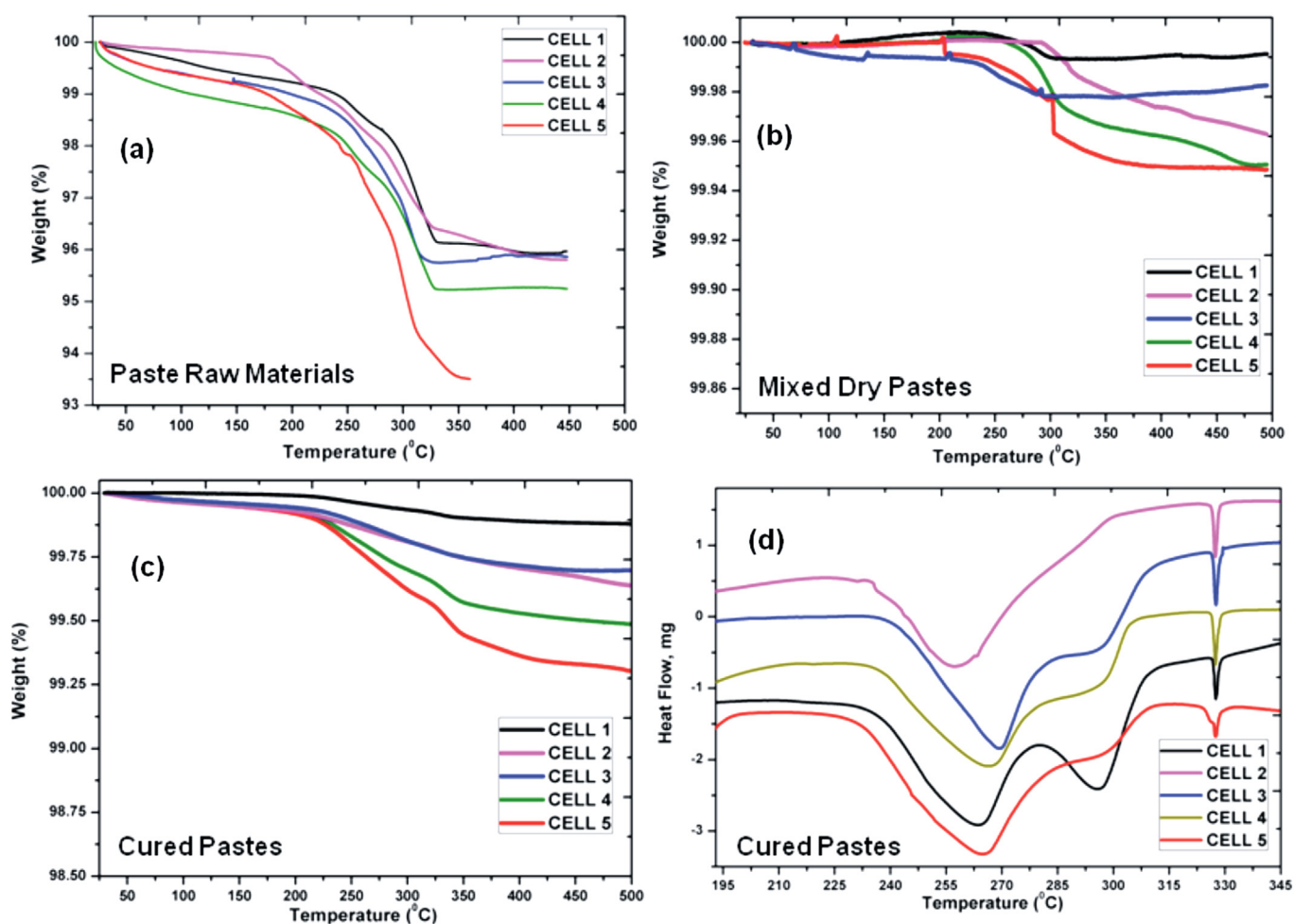


Fig. 3. TG curves for (a) paste raw material, (b) mixed dry paste, (c) cured paste, (d) DSC curves for cured paste.

were disconnected and opened). In this study all the NAM samples are taken from the centre of the negative plate and prior to analysis, the cycled NAM samples are washed with DI water and dried. The NAM particles tend to be connected due to the sugar carbonization and the particle sizes were slightly reduced compared with CB added NAM as shown in Fig. 4b. This might be the influence of temperature on the lead oxide particles (melting point of Pb is 327 °C). The degree of oxidation of the LO was depend on the production method (Barton-pot or ball-mill process), which ensures the quantity of free lead availability. Reducing the particle size is an effective way of increasing the surface area and decreasing the diffusion distance for charge transfer. SDC incorporated NAM form new lead nuclei during the formation processes as shown in Fig. 5b and inset. The NAM surface is covered with SDC which enhances the high rate charge and discharge reactions. This kind of prominent structure creates a new electrochemically active interface [21,45].

3.1. Charge–discharge studies

In order to determine nominal capacity of the cell after its formation step, the cell was subjected to four charge/discharge cycles (20 h of discharging mode, 0.05C). The charging was performed for 110% of nominal capacity. Subsequently, the cell was subjected to C₁₀ (30 cycles) and C₄ (5 cycles) as shown in Fig. 6a. These results confirm that the active material utilization was improved by the addition of SDC into NAM. Interestingly, the plate with leady oxide

with sugar dissolved in water (Cell 4) showed the highest discharge capacity in our experimental range. Cell 1 exhibited the poor response and only 48% of the active material was utilized. Cell 2, 3, and 5 exhibits 50 to 53% of active material utilization (Fig. 6a -inset). The best electrochemical response was obtained for Cell 4, which consisted of well combined in-situ formed conductive additive and it showed highest utilization of the active material (about 60%). This suggests an improved electrically conductive path combined with porosity leads to higher amount of acid present in the vicinity of the active-material particles which is responsible for the highest utilisation of active material.

It can be observed that the CB added cell (Cell 1) has a low discharge capacity of nearly 850 mAh while the Cell 2 to Cell 4 delivered a relatively high discharge capacity of 950 mAh–1120 mAh respectively. The much higher discharge capacity of the SDC added cells in comparison with the CB added cell could be attributed to the following reasons: SDC was impregnated with leady oxide at various synthesis condition can provide conductive connections between the active particles which are favourable to the electron transfer and the smaller particle size of the active materials can shorten the diffusion path and this can significantly decrease the inter particle resistance resulted in improved rate performance. However, the Cell 4 delivers a relatively higher capacities and better rate capability in comparison with the other cells. Since the water has much higher solubility for sugar than alcohol at ambient temperature, the active mass synthesis with water medium displayed remarkably improved homogeneity of the additive, creates the appropriate pores and

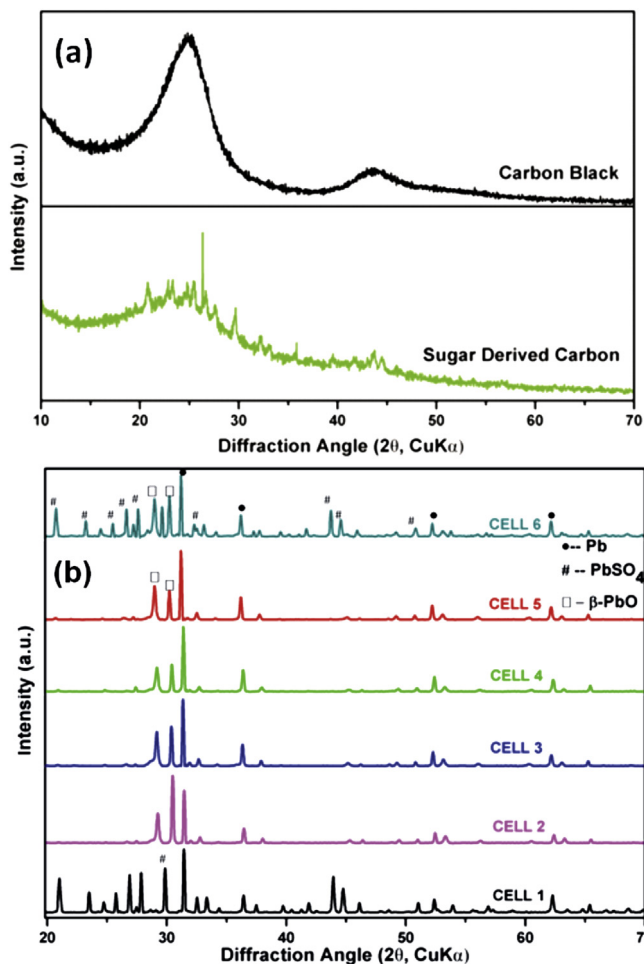


Fig. 4. XRD patterns of (a) carbon black and sugar derived carbon, (b) formed state NAM.

improves the active mass accessibility. We found that the SDC can minimize the particle growth during the in situ forming process and increase the electronic conductivity of the NAM remarkably. The capacity of Cell 6 declines rapidly. This result indicates that the electrochemical performance is determined by not only heat treatment of leady oxide. It is associated with in situ formation of conductive additives. Fig. 6b depicts the charge–discharge voltage profiles for the CB and SDC added cells at 10 h rate. Large polarization during charging has always been identified as a significant problem in achieving a high rate performance. The polarization is significantly reduced in SDC added cells as compared with control cell which favours the charging process has become more reversible. Conductivity of the active mass is an important factor which manipulates polarization in electrode materials.

3.2. Accelerated PSoC cycling

Change in end-of-charge/discharge voltage during the APSoc run is shown in Fig. 6c. The cell voltage was measured in every

Table 1
Specific characteristics of the SDC.

Description	Specific characteristics
Density	0.35 (g/cc)
Avg. particle size	2–8 μm
BET	457 m ² g ^{−1}

Table 2
Summary of paste density, penetration and surface area.

Cell num	BET (m ² g ^{−1})	Density (g inch ^{−3})	Penetration
Cell 1	1.9	74	22
Cell 2	3.1	70	24
Cell 3	6.3	71	23
Cell 4	19.98	72	23
Cell 5	9.8	72	23

100th charge/discharge cycle. It can be seen that the Cell 4 showed the best performance in the APSoc cycling. The data are reminiscent of the synthesis condition in which sugar is dissolved with deionised water for the preparation of a sugar solution and heated with leady oxide that provide low resistant pathways and short distance for ions through the porous particle in negative lead electrodes that hinders the growth of lead sulfate crystals. This implies that the surface level activation of the carbon material plays

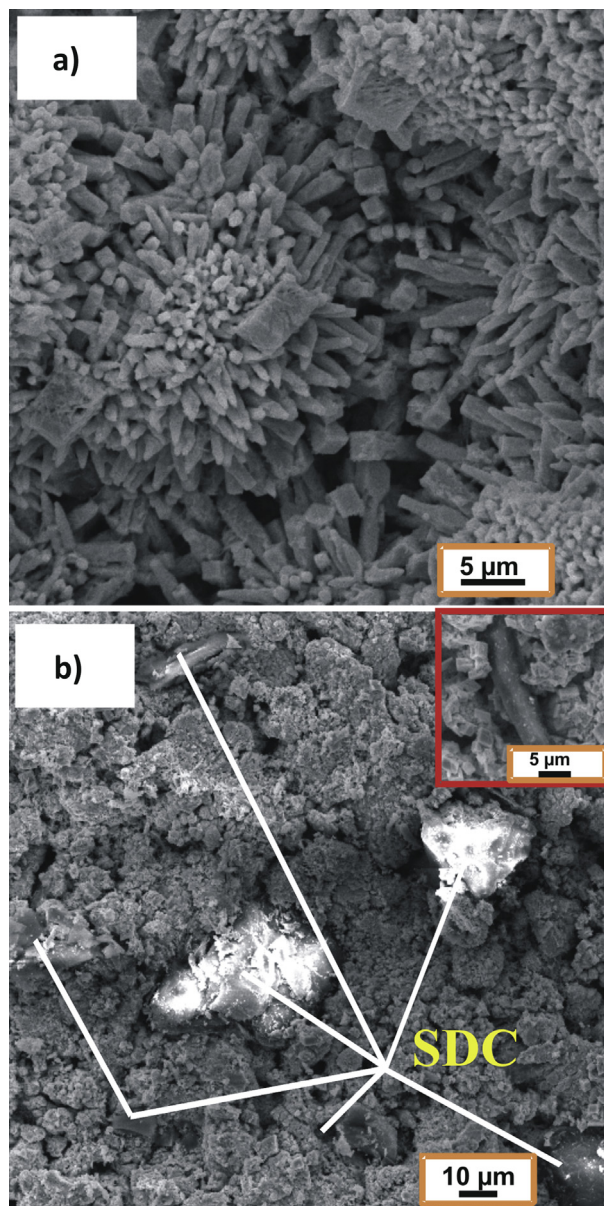


Fig. 5. SEM images of (a) CB, (b) SDC incorporated NAM partially formed state.

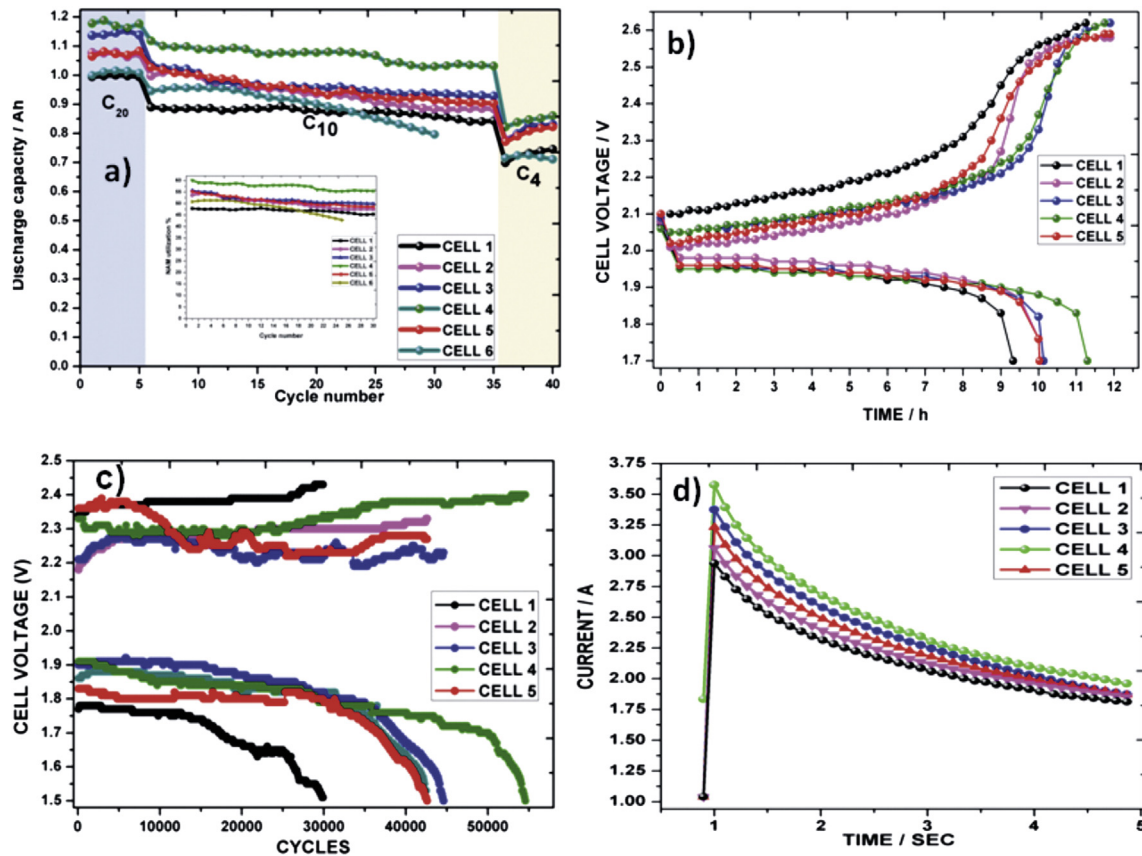


Fig. 6. (a) Discharge capacities of at different current densities, (b) galvanostatic charge–discharge profiles in 10 h rate, (c) end-of-charge/discharge voltage during APSOC run, (d) charge acceptance curves.

a significant improvement on the cell performance when operated in APSOC cycling (Fig. 6c).

Addition of SDC has a significant effect on the charge kinetics. Moreover, Cell 2 to Cell 4 demonstrate a significantly longer and flatter discharge behaviour than that of the Cell 1 which should be attributed to superior electrical conducting characteristics of SDC and the lower degree of polarization, improving the charge acceptance of the electrode materials during the electrochemical reaction. The polarization is significantly reduced showing that the charge process has become more reversible. On the contrary, the higher electrochemical polarization of Cell 1 suggests the lower conductivity is caused by the carbon black to NAM which cannot form an effective conducting network and results in the end of life of cell marked with a steep voltage drop caused apparently by a lead sulfate layer at the plate surface as shown in Fig. 6c. Moreover, a high lead sulfate layer in the NAM that provokes a large electrode polarisation on charge that leads the evolution of hydrogen and cell drying out [46]. The thermo treated lead oxide with SDC promotes the formation of a highly effective conducting pathway between

the lead/lead sulfate particles, resulting in the lower polarization and full availability of spongy lead as active materials during the APSOC process. It has been concluded that the improved APSOC performance is due to small particle size and enhanced electronic conductivity of NAM. Table 3 shows the number of completed cycles at APSOC run. It can be seen that the number of completed cycles declines considerably after each cycle set. Most probably, oxidation of some form of carbon by the evolved oxygen which shortens the cycle life of cells [22]. Another possible reason may be migration of carbon particle in the interior of the electrodes [47]. This effect may be involved in our cells and the exact mechanism is unclear.

3.3. Charge acceptance test

In present day HEV applications, batteries operated in the PSoC condition should accept the charge from regenerative braking. The negative plates of LAB have low charge acceptance when cycled at high rates. Moreover, the high rate charging which is required in HEV applications is usually only for few seconds. In this study, the test cells were subjected to 5-s of the high rate charge (3C) with an upper voltage limit of 2.55 V. The maximum initial peak current was attained in the Cell 4 compared with other cells. It can be expected that there is an optimum quantity of interconnected electronic network between discharged product of PbSO₄ and SDC particles, which ensures the higher initial charge current compared with CB added NAM as shown in Fig. 6d. However, the higher initial charge current leads the formation of a tiny number of small Pb crystals rather than a large number of big crystals, which is decisive to build up the energetic structure of the NAM [48]. Thus in situ

Table 3
Number of completed cycles at APSOC run.

Cell num	Cycle life in 1st run	Cycle life in 2nd run	Cycle life in 3rd run	Cycle life in 4th run
Cell 1	29,878	22,297	16,833	8994
Cell 2	42,576	35,323	28,234	20,158
Cell 3	44,502	38,672	34,204	29,456
Cell 4	54,500	48,902	44,978	41,457
Cell 5	42,574	36,288	33,108	30,956

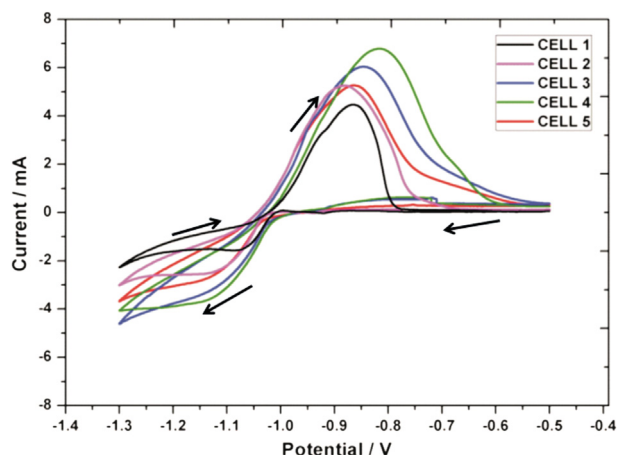


Fig. 7. Cyclic voltammograms (vs. MMS electrode) scan rate = 5 mV s^{-1} ; electrolyte = $1.28 \text{ g cm}^{-3} \text{ H}_2\text{SO}_4$.

formed SDC with leady oxide offers a promising approach towards enhancing the charge acceptance and cycle life of negative plates in lead-acid cells.

3.4. Cyclic voltammetry

In order to further understand the electrochemical properties, the cyclic voltammetry (CV) was performed at a scan rate of 5 mV s^{-1} at room temperature as shown in Fig. 7. Each of the CV curves consists of an oxidation peak and a reduction peak, corresponding to the charging reaction and discharge reaction of the Pb/Pb^{2+} redox couple. These results point out interesting features of the cyclic voltammetry behaviour when the sugar SDC is present with respect to CB. The anodic peak current is comparatively higher than carbon black with a shift of the peak-potential slightly towards positive values. The shift towards more positive potentials is not significant and it is kinetically hindered. Impedance studies reveal smaller charge transfer resistance which may be one of the reasons for the improved performance. Among the SDC with LO, carbon derived from sugar in water as solvent shows higher peak current indicative of higher utilisation of LO. Some modifications are also

visible on the cathodic branch. In the presence of SDC with LO, the cathodic peak is broader and presents some shift compared to carbon black.

3.5. Scanning electron microscopy of NAM after charge/discharge cycles

Fig. 8a shows SDC in the non-milled form with irregular morphology with a particle size of $\sim 2\text{--}8 \text{ }\mu\text{m}$. Fig. 8b–e demonstrates that the SEM images of CB and SDC added NAM after 22,000 cycles of first APSOC run. It was found that CB added NAM fully covered with lead sulfate particles as shown in Fig. 8b. This type of lead sulfate cannot, or only partially, be reconverted back to an electrochemically active form. If the discharged NAM contains large crystals of lead sulfate, then conversion of this material to lead in the early stages of charging will become difficult [49]. This observation suggests that the performance declines gradually due to accumulation of lead sulfate. It can be seen (Fig. 8c–f) that very little lead sulfate has accumulated during APSOC cycling and the NAM surface is almost completely covered by SDC particles that appear as bright spots. Consequently, the electrochemical reaction may proceed on the lead/SDC surface. This surface acts as electrocatalyst to the charge reaction [21]. Moreover, sulfuric acid plays an efficient dehydrating agent to turn sugar to carbon [27].

Fig. 8d shows that long fibre morphology formation which enhances the structural orientation and conductivity of NAM. A possible mechanism for the formation of fibre form may be due to sugar that has been melted and solidified at mild temperature yielded as self arranged fibre morphology with NAM. Fig. 7e reveals that the sugar was fully dissolved with deionised water and heated with leady oxide, so that uniform formation of intra particle contact with active material is realized, which is well in agreement with particle size of SDC. This material has a uniform distribution of small particle size and all particles are uniformly covered with sugar carbon. The possible mechanism is that the water addition leads to the porous structure may allow electrolytes to gain easy access to the interior of the electrode, leading to a higher discharge capacity and APSOC cycling performance. Interestingly, this synthesis condition prevents the biggest lead sulfate crystals in the NAM under APSOC cycling as shown in Fig. 8e. To identify the particle size of the sugar, it has dispersed in a same quantity of

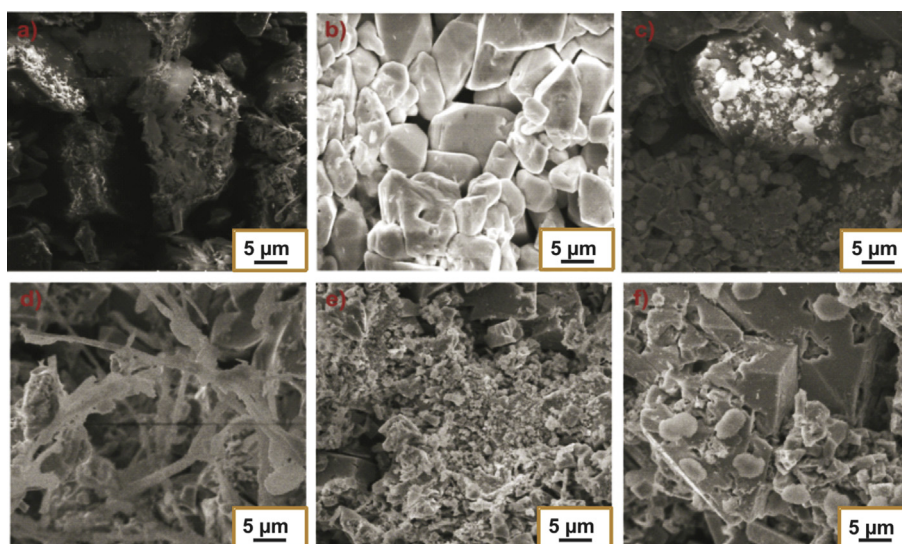


Fig. 8. SEM images for (a) sugar derived carbon, (b) NAM with CB, (c) NAM with post heat treated sugar derived carbon, (d) NAM with sugar heat treated, (e) NAM with water as a solvent for sugar heat treated and (f) NAM with alcohol as a solvent for sugar heat treated (after 22,000 cycles of APSOC run).

alcohol and water solution. Subsequently, the dispersed solutions are measured for particle size by dynamic laser light diffraction from the samples [47]. The obtained values are 1340 nm and 625.8 nm respectively as shown in Fig. 9a and b. Probably the solubility of sugar followed by its conversion into carbon during heating leads to much smaller particle. Thus the plates prepared by this method (Cell 4) performed well in APSOC cycling. Thus, smaller PbSO_4 crystals are formed, which have higher solubility and sustain higher Pb^{2+} ion concentration in the solution, thus supplying sufficient amount of Pb^{2+} ions for the charge process [7]. The morphology of the NAM was also strongly dependent on the type of carbon content. The particle size of CB added cell was the biggest among the five samples. The Cell 4 consisted of much smaller particles with size less than 2–3 μm . Nevertheless, it can be clearly observed that CB added NAM had a much larger particle size, compared to that of SDC added NAM. The results confirm the well-known fact that the higher specific surface area is responsible for the increased capacity of the active material. The morphological analysis was in good agreement with the XRD analysis results. It

was reasonable to assume that the SDC covered on the surface of NAM particles could not only inhibit particle growth but also improve electrical conductivity. Furthermore, the additives are effective in changing the distribution of PbSO_4 in the discharged NAM from the surface to the interior. The structure of SDC contributes to the form of network within the NAM, which can interconnect the isolated particles, so that the electrons can be readily transmitted to the sites where reduction reactions take place easily. The results indicated that the SDC particles (white dots) were uniformly distributed in the active material, which would effectively control the volume change of active material during the dissolution/deposition process. In order to identify the presence of carbon (white dots and flakes) in the cycled NAM, further it has been subjected to Energy-Dispersive X-ray Spectrometry (EDS). Fig. 10a shows the CB added NAM, in which there is no obvious peak assigned to carbon. Interestingly, a high level of carbon peak present in the SDC added NAM (Fig. 10b). Based on the obtained EDS results it can be concluded that the SDC presents as in situ with NAM.

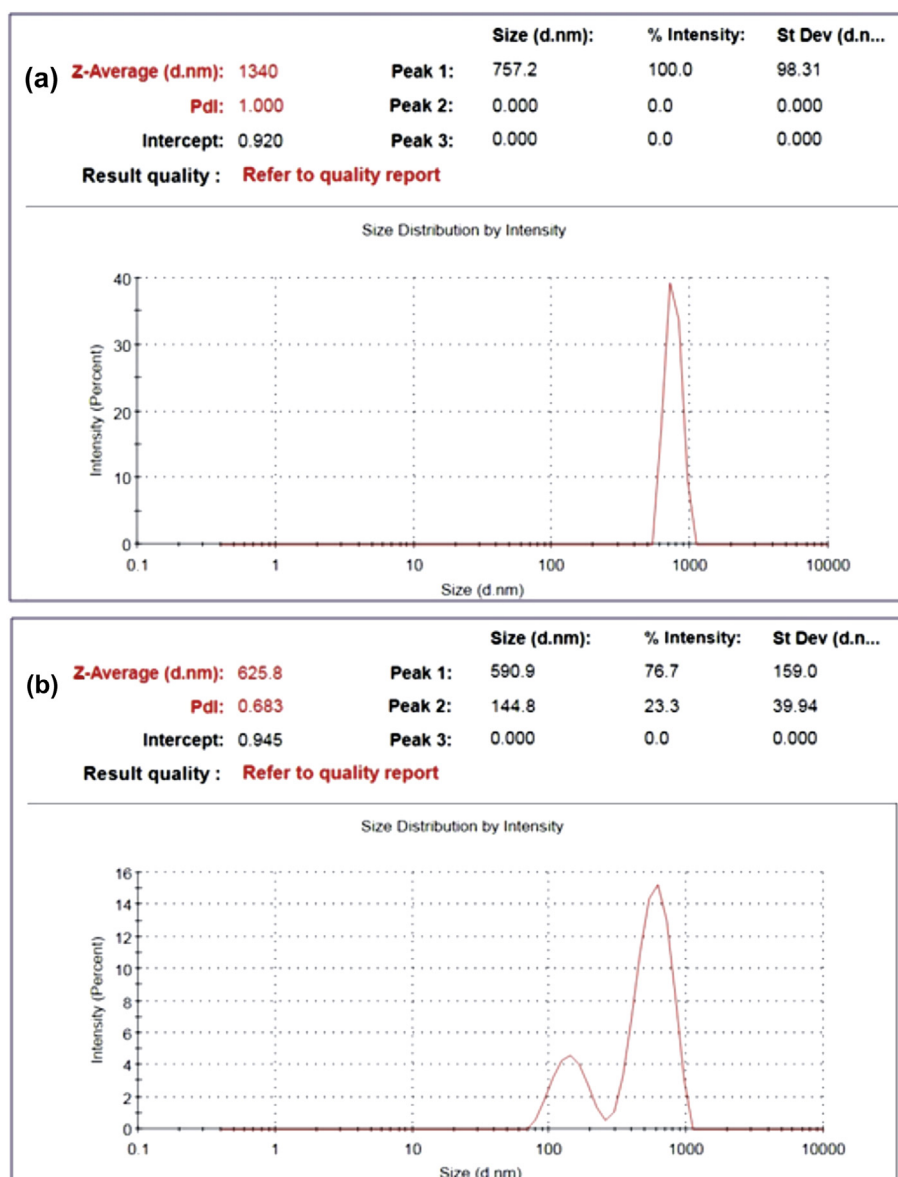


Fig. 9. DLS results of sugar dispersed in (a) alcohol, (b) water.

3.6. Impedance measurement

Fig. 11 shows the impedance measurements for the cells carried out with an AC amplitude of 10 mV over a frequency range from 100 kHz to 10 mHz. The semi circles in the Nyquist plots are depressed which may be due to the change in the resistive and capacitive components of electrode/electrolyte interface with electrode position, electrode non uniform thickness etc., [50]. SDC added cells showed a smaller charge transfer resistance compared with carbon black added cell as shown in Fig. 8. The decrease in charge transfer resistance could be related to the affinity of sugar carbon with lead particles. It is well known that a small charge transfer resistance is important for a negative electrode to obtain good electrochemical performance.

3.7. XRD characterization of NAM after charge/discharge cycles

Fig. 12a shows a comparison of the XRD-patterns of the partially discharged state of NAM (after 22,000 cycles of first APSoc run) with typical materials containing lead and lead sulfate in the Cells 2–5. In the Cell 1 major part accomplish by lead sulfate and very weak peaks which can be assigned to lead. Intensity of the diffraction peaks values is indexed in the XRD pattern. SDC can be readily and independently controlled by the synthesis condition with LO is a crucial role and prevent the large lead sulfate crystal and the reduction process take place much easily under APSoc condition. In addition during the synthesis process leady oxide was heated up to 300 °C for 2 h, and this kind of heat treatment is not affected the crystalline nature of the samples as well documented in XRD results. On the other hand, the fact that the lattice parameter does not increase with rising the heating temperature this is

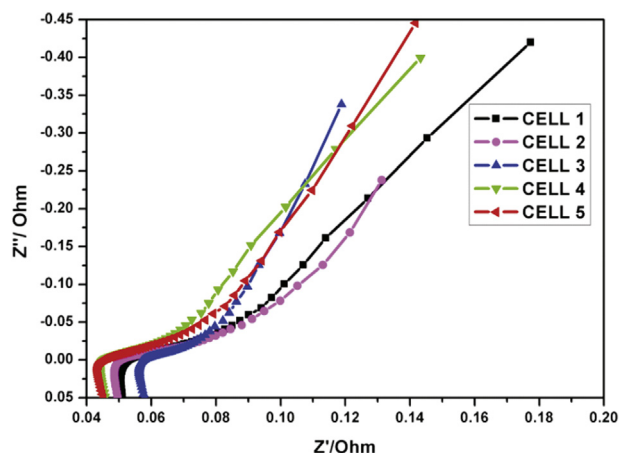


Fig. 11. Electrochemical impedance spectra for CB and sugar derived carbon added plates.

probably due to the very short thermal treatment time (2 h). The decrease of lead sulfate diffraction peaks indicates that SDC added NAM consisted of relatively smaller particles than CB added NAM, which could be related to the suppression of continuous growth for PbSO_4 particle. Pavlov et al. have made extensive studies on PbSO_4 crystallinity by intensity of the diffraction peak [51,52]. In the present work we have calculated the intensity of diffraction peak

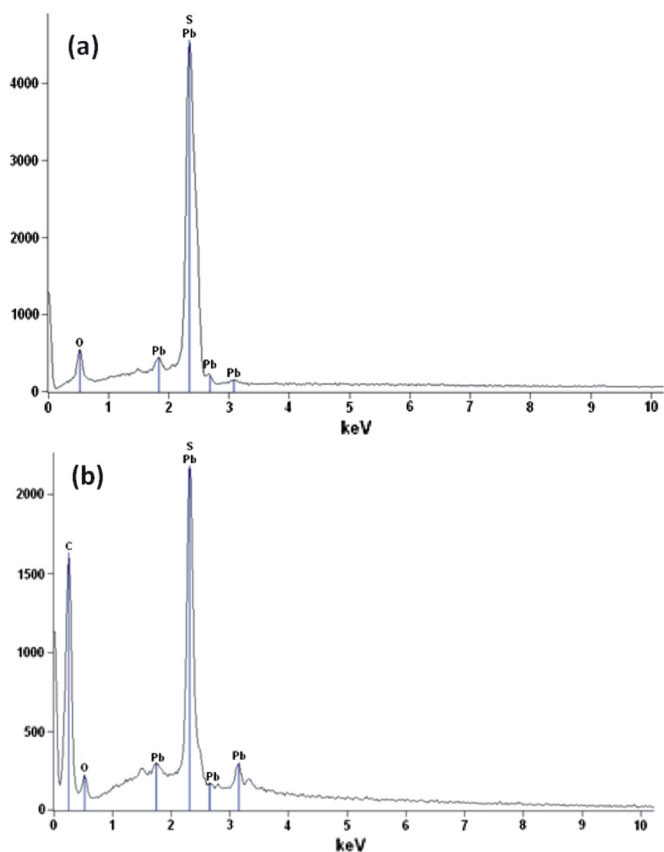


Fig. 10. EDX spectroscopy of (a) CB added NAM, (b) SDC added NAM.

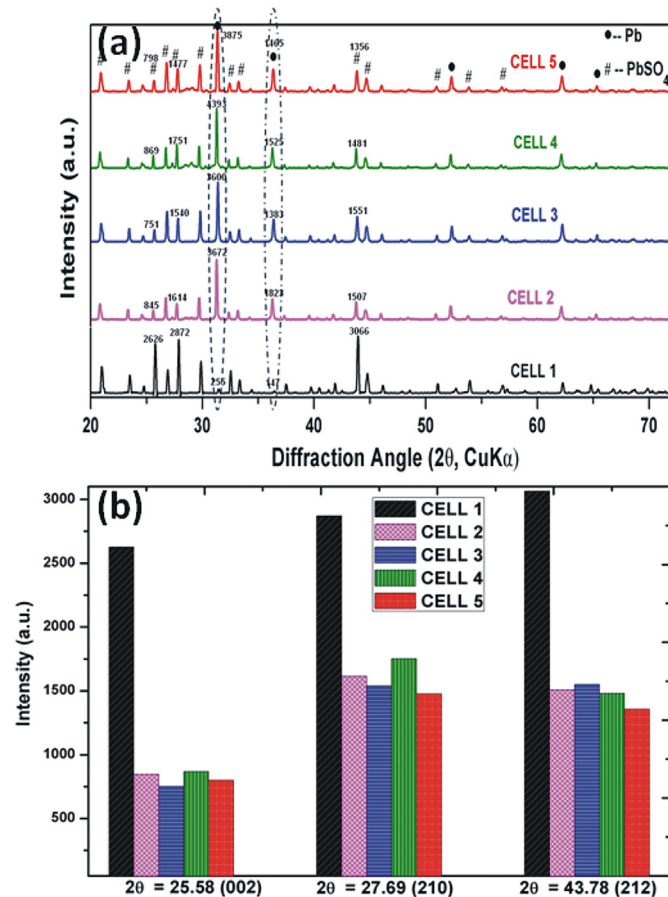


Fig. 12. (a) Powder X-ray diffraction pattern of partially discharged NAM (after 22,000 cycles of APSoc run), (b) intensity of the diffraction peaks at $2\theta = 25.58^\circ$ (002), 27.69° (210) and 43.78° (212) for PbSO_4 crystals.

values from the XRD pattern as shown in Fig. 12b. Among the 2θ range, we have selected three highest intensity peaks for PbSO_4 [$2\theta = 25.58^\circ$ (002), 27.69° (210) and 43.78° (212)]. It is worth noting that the intensity of the PbSO_4 diffraction peak is twofold higher and a highly crystalline lead sulfate has formed in the CB added NAM. These types of crystals are more difficult to reduce during APSOC cycling. This observation probably implies the recrystallization and reversibility of the electrochemical behaviour of SDC added NAM. This is responsible for the high performance electrode material in the PSOC cycling. Moreover, there are no obvious carbon diffraction peaks in the NAM due to its low content.

4. Conclusions

It has been proved that SDC could attract much attention for the development of lead acid batteries. It is clear that, in situ formed sugar carbon with leady oxide to the NAM has the ability to suppress the formation of a lead sulfate layer on the plate surface. We believe that, in negative-plate technology there are strong prospects that greatly elevated levels of in situ formed SDC with leady oxide will soon take an ameliorate place in industry standard protocol. It is suggested that the dispersion of the conductive additive in the active mass plays a crucial role in the electrochemical performance of cell and greatly enhances the active mass utilization depending on their synthesis processes. The SDC has become integrated into the NAM and greatly enhances the electrochemical performance mainly due to its low ohmic resistance between lead particles to lead particle contacts. Moreover, this contact makes the charge/discharge reaction much easier even at high rates and leads to the better charge acceptance. Therefore, SDC embedded active material could be employed as a promising, safe, cheap candidate negative plates for lead acid battery after further modification.

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